



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C07C 43/225, 43/174, 323/09 C08F 16/12, 128/04		A2	(11) International Publication Number: WO 90/15043 (43) International Publication Date: 13 December 1990 (13.12.90)
(21) International Application Number: PCT/US90/03154 (22) International Filing Date: 4 June 1990 (04.06.90)		(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent).	
(30) Priority data: 364,665 9 June 1989 (09.06.89) US		Published <i>Without international search report and to be republished upon receipt of that report.</i>	
(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).			
(72) Inventors: BABB, David, A. ; 419 Narcissus, Lake Jackson, TX 77566 (US). CLEMENT, Katherine, S. ; 126 Daisy, Lake Jackson, TX 77566 (US). EZZELL, Bobby, R. ; 1310 Ashly court, Midland, MI 48640 (US).			
(74) Agent: PRIETO, Joe, R.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).			

(54) Title: PERFLUOROVINYL COMPOUNDS

## (57) Abstract

The present invention is directed to compounds having at least two perfluorovinyl groups and having a structure represented by the following formula (I):  $CF_2=CF-X-R-(X-CF=CF_2)_m$ , wherein R represents an unsubstituted or inertly substituted hydrocarbyl group; each X is independently selected from the group consisting of groups having at least one non-carbon atom between R and  $-CF=CF_2$ ; and m is an integer of from 1 to 3. Polymers formed from such compounds are also prepared. The compounds are preferably prepared by a process comprising the steps of: (a) forming a salt having anion corresponding to a compound of the following formula (II):  $HX-R-(XH)_m$ , wherein X, R and m are as defined for formula (I); (b) reacting the salt formed in step (a) with a 1,2-dihalo-1,1,2, 2-tetrafluoroethane wherein the halo groups are iodine, bromine, chlorine or mixtures thereof, at least one halo group being bromine or iodine, to form a compound of the following formula (III):  $Z-CF_2CF_2-X-R-(X-CF_2CF_2-Z)_m$ , wherein X, R and m are as defined for formula (I) and each Z is independently iodine or bromine; and (c) eliminating the halogen atoms represented by Z to form the perfluorovinyl compound represented by formula (I).

## DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

### FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MC	Monaco
AU	Australia	FI	Finland	MG	Madagascar
BB	Barbados	FR	France	M.	Mali
BE	Belgium	CA	Gabon	M	Mauritania
BF	Burkina Fasso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GR	Greece	NL	Netherlands
BJ	Benin	HU	Hungary	NO	Norway
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	SD	Sudan
CF	Central African Republic	KP	Democratic People's Republic of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SN	Senegal
CH	Switzerland	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
DE	Germany, Federal Republic of	LU	Luxembourg	TC	Togo
DK	Denmark			US	United States of America

-1-

## PERFLUOROVINYL COMPOUNDS

This invention relates to compounds having at least two perfluorovinyl groups; to a process for preparing the perfluorovinyl compounds to a process for preparing the perfluorovinyl compounds and to a process 5 for polymerization of the perfluorovinyl compounds.

Certain compounds having a perfluorovinyl group have been prepared by a variety of methods such as those disclosed in U.S. Patent 2,671,799 to Miller; U.S. 10 Patent 3,277,068 to Wall et al.; Prober in J. Amer. Chem. Soc. v. 75 (1953) pp. 968-973; Hodgdon and Macdonald, J. Polymer Sci. Part A-1, v. 6 (1968) pp. 15 711-717; Heinze and Burton, J. Org. Chem. 1988, 53, 2714-2720 and references cited in these references.

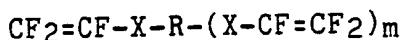
Certain alkyl or aryl 1,1-difluoroalkyl ethers such as 1,1,2-trifluoro-2-chloro-2-iodoethyl phenyl ether are prepared by reacting an alkoxide or phenoxide 20 with certain 1,1-difluoro-1,2-dihaloethanes under conditions disclosed in U.S. Patent No. 4,423,249 issued to Carl and Ezzell. In the same reference certain of the 1,1-difluoroalkyl ethers are disclosed to be

-2-

dehalogenated using zinc to form the corresponding vinyl ethers.

In one aspect, the present invention is a compound having a structure represented by the following Formula I:

5      Formula I

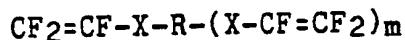


wherein R represents an unsubstituted or inertly 10 substituted hydrocarbyl group; each X is independently selected from the group consisting of oxygen atoms, sulfur atoms, sulfoxide, sulfone, carbonyl, thiocarbonyl and silanediyl groups; and m is an integer of from 1 to 3.

15

In yet another aspect, the present invention is a process for preparing compounds of the following Formula I:

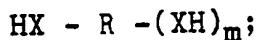
20      Formula I



wherein each X is independently -O-, -S-, -SO<sub>2</sub>- or -SO-; and R is a hydrocarbyl group, which group is 25 unsubstituted or inertly substituted, by a process comprising the steps of:

(a) forming a salt having anion corresponding 30 to a compound of the following Formula II:

Formula II



wherein X, R and m are as defined for Formula I;

-3-

(b) reacting the salt formed in step (a) with a 1,2-dihalo-1,1,2, 2-tetrafluoroethane wherein the halo groups are iodine, bromine, chlorine or mixtures thereof, at least one halo group being bromine or iodine to form a compound of the following Formula III:

5      Following III

$Z-CF_2CF_2-X-R-(X-CF_2CF_2-Z)_m$   
wherein X, R, and m are as defined for Formula I, and each Z is independently iodine or bromine; and

10     (c) eliminating the halogen atoms represented by Z to form the perfluorovinyl compound represented by Formula I.

15     In yet another aspect, the present invention includes polymers of compounds of Formula I.

20     The monomers of the present invention preferably have a structure represented by the following Formula I:

Formula I

25      $CF_2=CF-X-R-(X-CF=CF_2)_m$

wherein R represents an, optionally inertly substituted, hydrocarbyl group; each X is independently a bond or any group which links R and a perfluorovinyl group

30     (hereinafter linking structures), said structures being inert; m+1 is the number of  $-X-CF=CF_2$  units. Advantageously, m is an integer of from 1 to 3, preferably from 1 to 2. By "inert" it is meant that the structures or substituents do not react undesirably with perfluorovinyl groups or interfere undesirably with

-4-

polymerization (perfluorocyclobutane formation) of the monomers.

Linking structures X are each independently a linking structure such as a bond, an oxygen atom, carboxylic and thiocarboxylic ester groups, other sulfur containing structures, perfluoroalkylene, perfluoroalkylene ether, alkylene, acetylene, phosphorus containing groups such as phosphines, carbonyl and thio carbonyl groups; seleno; telluro; nitrido; silicon-containing groups such as silanediyl, trisilanediyl tetrasilanetetrayl, siloxanediyl, disiloxanediyl, trisiloxyl, trisilazanyl, or silylthio groups; boron-containing groups such as boranediyl or methylboranediyl groups; a combination thereof, or any other group which is inert, which molecularly links R to a perfluorovinyl group, and which provides a molecular structure in which the perfluorovinyl group is sufficiently reactive to form a perfluorocyclobutane ring. For instance, X is preferably other than a perfluoroalkylene groups because perfluorovinyl groups attached to perfluoroalkylene groups generally require temperatures greater than about 300°C to dimerize and are subject to isomerization.

It is preferred that at least one of X is not a bond. More preferably, X is independently selected from the group consisting of groups having at least one non-carbon atom between the perfluorovinyl groups and R, such as groups containing oxygen, sulfur, selenium atoms, tellurium atoms, silicon, boron, phosphorus or nitrogen between R and the perfluorovinyl group, for example oxygen atoms, sulfur atoms, (thio) carboxylic ester groups, phosphines, (thio) carbonyl groups, seleno, telluro, silanediyl, trisilanediyl, trisilazanyl

-5-

or silylthio, boranediyl groups. Preferred groups have S, O, Si, N or P, more preferably S, O, or Si between R and the perfluorovinyl group, such as carbonyl, thiocarbonyl, sulfone, sulfoxy, silanediyl, amines (optionally inertly substituted), oxygen or sulfur atoms. Most preferably X is a single atom other than carbon; even more preferably it is oxygen or sulfur, among those groups preferably an ether or sulfide linkage, because monomers having such linking structures advantageously form perfluorocyclobutane groups at lower temperatures than are needed with such groups as perfluoroalkyl groups and are more stable than monomers where the perfluorovinyl group is attached directly to R, particularly when R is aromatic. Monomers having such linking structures are also relatively easily prepared.

R is suitably any inert hydrocarbyl molecular structure, preferably a molecular structure which facilitates formation of perfluorocyclobutane rings and/or imparts desirable physical properties to polymers or oligomers prepared from the monomers. For the purpose of imparting desirable physical properties to polymers, R preferably contains at least one carbon atom. Preferably, the carbon atom is in the molecular chain between X's because monomers having at least one carbon atom between X's when each X is other than a bond, tend to have desirable stability and to produce polymers having desirable physical properties. Alternatively, the carbon atom is in a side chain; for instance, -R- can be -N(CH<sub>3</sub>)-, -N(CH<sub>2</sub>CH<sub>3</sub>)-, -P(CH<sub>3</sub>)-, or -P(CH<sub>2</sub>CH<sub>3</sub>)-. The carbon atoms(s) in R are suitably in aliphatic, cycloaliphatic, aromatic, heterocyclic groups and the like and combinations thereof. R is preferably

a hydrocarbyl group, that is a group containing at least one carbon hydrogen bond, for instance a methylene group, a phenylene group or a pyridinyl group.

Additionally, R optionally contains groups or has substituents which are inert, that is which do not undesirably interfere with the formation of 5 perfluorocyclobutane rings from perfluorovinyl groups. Inert substituents include ether, carbonyl, ester, tertiary amide, carbonate, sulfide, sulfoxide, sulfone, nitrile, alkyl phosphonate, tertiary amine, alkyl 10 phosphate, alkyl silyl, chlorine, bromine, fluorine, alkyl, arylalkyl, alkylaryl, cycloalkyl, aromatic, heterocyclic, alkoxy, aryloxy groups and the like, which inert substituents are suitably in any position, for instance, in a polymer backbone between X's and/or 15 appended to such a backbone. Carbon-containing inert substituents on R preferably contain from 1 to 50, more preferably from 1 to 12 carbon atoms because of the stability and ease of working with monomers of lower molecular weight. R, including inert substituents 20 preferably has a molecular weight (MW) of from 14 to 20,000, more preferably from 75 to 15,000 and most preferably from 75 to 5,000. These ranges include monomeric and oligomeric R groups. In the case of 25 monomers which are other than oligomeric, R preferably has from 1 to 50, more preferably from 6 to 50, carbon atoms because molecular weights above this reduce the contribution to properties made by the fluorine-containing substituents. The nature of R as well as the 30 perfluorocyclobutane content of the polymers can vary broadly according to the type of products desired.

Preferably, for polymers having good plastic properties such as tensile strength and flexibility, at

least one carbon atom of R is in the molecular chain between X's and is part of an aromatic nucleus. Aromatic groups are desirable because of improved physical properties of the polymers and ease of manufacture of the monomers. For both ease of 5 manufacture of the monomer and monomer stability, when R is aromatic, each X is preferably independently sulfur or oxygen. The aromatic group can be any molecular structure having aromatic character, advantageously having at least one six membered aromatic ring, suitably 10 having any number of such six-membered rings fused together or connected by bonds or linking structures. R preferably has from 1 to 50 such rings, more preferably from 1 to 10 rings, more preferably containing from 6 to 25 carbon atoms, most preferably R 15 has at least 2 to 4 aromatic rings to impart properties such as hardness and/or stiffness to a polymer. The aromatic fragment is suitably unsubstituted or inertly substituted. Inert substituents on an aromatic R 20 include, for instance, the inert substituents listed for R generally. Exemplary aromatic molecular fragments include, for instance, perchlorophenylene, phenylene, biphenylene, naphthylene, dichlorophenylene, nitrophenylene, p,p'-(2,2-diphenylene propane) [-C<sub>6</sub>H<sub>4</sub>-C(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>]; p,p'-(2,2-diphenylene-1,1,1,3,3,3 25 hexafluoropropane) [-C<sub>6</sub>H<sub>4</sub>-C(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-], preferably biphenylene; phenylene; 9,9'-diphenyl-fluorene, oxydiphenylene; thiodiphenylene; 1,3,5-triphenylene-benzene; 1,3,5-(2-phenylene-2--propyl)bezene; 30 1,1,1-triphenylenemethane; 1,1,2,2-tetraphenylene-1,2-diphenylethane; bis(1,1-diphenyleneethyl)benzene; 1-(2-phenylene-2-propyl)-4-(1,1-diphenylene ethyl)benzene; 1,1,1-triphenyleneethane; 2,2-diphenylene propane; 2,2'-diphenylene, 1,1,1,3,3,3-hexafluoro-

-8-

propane; 1,1-diphenylene-1-phenyl ethane; naphthalene; and anthracene. Molecular weights of aromatic ring containing polymers are preferably at least about 10,000. Such aromatic groups are preferably present because they generally impart high temperature glass transition properties (Tg) and good mechanical strength (for example as measured by differential scanning calorimetry (DSC) and tensile/flexural tests) to the polymer.

10            Most preferably, at least one aromatic carbon atom of R is bonded directly to X, most preferably aromatic carbon atoms of R are bonded directly to each X because perfluorovinyl groups bonded to X, said X being bonded to aromatic groups are generally more reactive in 15 forming perfluorocyclobutane rings.

20            Some specific combinations of X and R are especially preferred: when R is aromatic, at least one X is preferably other than a bond, more preferably neither X is a bond because attachment of perfluorovinyl groups directly to aromatic R renders the perfluorovinyl groups more thermally and oxidatively unstable than when said groups are attached. for instance to oxygen or sulfur.

25            Monomers useful in the practice of the present invention are suitably prepared by any method which links molecular structures having perfluorovinyl groups to other molecular structures or which form 30 perfluorovinyl groups. A variety of methods of preparation are suitable and are taught, for instance in copending U.S. Application Serial No. 364,667 filed June

-9-

9, 1989 and U.S. Patent Application Serial No. 364,666, filed June 9, 1989.

Compounds of Formula I are preferably formed by a process comprising the steps of:

5 (a) forming a salt having an anion corresponding to a compound of the following Formula II:

Formula II



wherein R, X and m are defined as for Formula I;

15 (b) reacting the salt formed in step (a) with a 1,2-dihalo-1,1,2, 2-tetrafluoroethane wherein the halo groups are iodine, bromine, chlorine or mixtures thereof, at least one halo group being a bromine or an iodine atom, to form a compound of the following Formula III:

20 Formula III

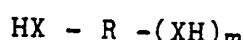


25 wherein R, X and m are defined as for Formula I; and each Z is independently iodine or bromine; and

(c) eliminating the halogen atoms represented by Z to form the perfluorovinyl compound.

30 Salts of compounds of the following Formula II:

Formula II



-10-

wherein R, X and m are as defined for Formula I; are suitably formed by any method which replaces the hydrogen atoms with metal cations. Suitable methods include reaction with bases such as sodium hydroxide or potassium hydroxide when the compound has an acidity reactive with a hydroxide, such as when R is aromatic or aromatic heterocyclic. Compounds which have acidify too low to react readily with a hydroxide are reacted, for instance, with metals such as sodium or their hydrides. among hydroxides, potassium hydroxide is generally preferred because potassium salts of alkoxides or aryloxides are more reactive than are lithium or sodium salts. Sufficient hydroxide or metal to form the salt is used, preferably from 1.0 to 2.0 equivalents of hydroxide of metal per equivalent of X in compounds of Formula II. Suitable temperatures and pressures are determined without undue experimentation and are conveniently atmospheric pressure and a temperature maintained below 140°C because oxidative degradation of some air-sensitive aryl oxides is enhanced at higher temperatures. Temperatures are preferably from 40°C to 125°C for an aromatic compound (R is aromatic) and of from -10°C to 125°C for an alkyl compound.

Suitably, both the compound of Formula II and the hydroxide are slurried or dissolved in an easily removeable medium such as methanol before reaction for ease of mixing the reactants. Alternatively, and preferably the hydroxide is mixed directly into a solution of the compound of Formula II in a solvent such as dimethylsulfoxide (DMSO) or dimethylformamide (DMF).

Alternatively, salts may be formed by reaction of compounds of Formula II with metals such as sodium or

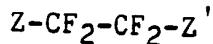
-11-

potassium or any metal which forms metal salts with compounds of Formula II; or with the metal salts of carbon acids such as the sodium salt of DMSO or the potassium salt of dimethylsulfone, preferably at temperatures of from -20°C to 200°C. These reactions are 5 particularly useful when R is alkyl or substituted alkyl. Use of metals is within the skill in the art and is found, for instance, in Introduction to Organic Chemistry, A. Streitwieser, Jr. and C. H. Heathcock, Macmillan Publishing Co., New York 1976, p. 216. Use of 10 metal salts of carbon acids is detailed in W. S. Matthews, et. al. J. Amer. Chem. Soc. 97:24 pages 7006-7014 (1975).

15 Although it is generally preferable for convenience, to maintain reactants in a slurry or solution for subsequent reaction, any liquid media, for example, methanol or glyme which is used as a solvent herein is suitably, alternatively, removed before the 20 next reaction step. Removal of protic media is necessary and removal is within the skill in the art. Methanol, for instance, is conveniently removed by rotary evaporation followed by heating to 100°C to 140°C under vacuum until the salt is dry.

25 The salt is then reacted with a 1,2-dihalo-1,1,2,2-tetrafluoroethane which is commercially available, or is prepared by reacting a halogen such as bromine or iodine with tetrafluoroethylene. The 30 dihalotetrafluoroethane has a structure represented by the following Formula IV:

Formula IV



-12-

wherein Z and Z' represent halogens other than fluorine. Z and Z' are preferably selected such that the tetrafluoroethane reacts readily with the anion leaving one halogen Z or Z', and that halogen is later readily eliminated to form a perfluorovinyl group. Z and Z' are, therefore, preferably selected from Cl, Br, and I 5 wherein at least one of Z or Z' is bromine or iodine; more preferably both Z and Z' are Br or I; most preferably both are Br. 1,2-dibromo-1,1,2,2-tetrafluoroethane is preferred because it is readily 10 available and undergoes elimination readily under suitable conditions.

The 1,2-dihalo tetrafluoroethane is preferably reacted with the salt in a liquid reaction medium which 15 is, for instance, suitably a solution or slurry of the salt in an aprotic solvent such as dioxane, dimethyl sulfoxide (DMSO), glyme, diglyme, tetraglyme, tetrahydrofuran, dimethylformamide or acetonitrile. 20 Polar aprotic solvents are preferred, with DMSO most preferred when the salt form of compounds of Formula II have low solubility. When the reaction medium is a slurry it is preferably stirred sufficiently to maintain the slurry and contact between the dihalo- 25 tetrafluoroethane and the salt. Sufficient solvent to homogeneously disperse both the dihalo-tetrafluoroethane and the salt is used, preferably from 0.01M to 10M concentration of salt of Formula II to use for convenience. Sufficient salt is reacted with the 30 dihalotetrafluoroethane to form a predetermined degree of substitution; preferably from 0.1 to 10.0 moles of salt per mole of dihalo-tetrafluoroethane is supplied, more preferably from 0.30 to 1.1 mole of salt. The dihalotetrafluoroethane is preferably added as a liquid.

The reaction temperature is preferably maintained above -30°C to achieve reaction at a convenient rate and below 100°C to avoid by-products. More preferably the temperature is maintained between 0°C and 50°C, most preferably between 20°C and 40°C when 5 R is aromatic and each X is independently -O-, -S-, -SO<sub>2</sub>- or -SO-; most preferably between about 0°C and about 20°C when R is alkyl. These temperatures are preferably used at atmospheric pressure which is preferably used for convenience. Alternatively sub- or 10 super-atmospheric pressure is used and temperature adjustments within the skill in the art are made. The temperature of the reaction is also dependent on the nature of any substituent group. In general, electron 15 donating substituents enhance the reaction, and cooling is necessary to keep the reaction temperature down. Electron donating substituents also activate the aromatic ring toward halogenation which can be a significant side reaction at elevated temperatures. The 20 reactions are preferably run at the lowest temperature possible to prevent ring halogenation. Electron withdrawing substituents, however, retard the reaction and deactivate the ring toward halogenation. Reactions involving deactivated phenols must be heated to obtain a 25 reasonable reaction rate. These can be heated much hotter than the activated phenols, since the deactivating groups also retard ring halogenation. In all cases the reaction is kept substantially free of 30 protic materials, which are preferably at concentrations of less than about 0.1 weight percent, most preferably in no detectable concentrations. Protic materials cause the production of an undesirable side product (that is -OCF<sub>2</sub>CF<sub>2</sub>H instead of -OCF<sub>2</sub>CF<sub>2</sub>Br). Protic materials include water, for example, alcohols and phenols.

-14-

The reaction of the salt and the 1,2-dihalo-  
tetrafluoroethane forms a 2-halo-tetrafluoroethyl  
compound of Formula III. The 2-halo-tetrafluoroethyl  
compound is either separated from the liquid media or  
further reacted in the media. Removal is by means  
5 within the skill in the art, such as by pouring the  
slurry into an equal volume of water and removing the  
product in a lower, oily layer which is then purified by  
vacuum distillation. If a liquid medium such as  
10 tetruglyme which does not dissolve completely in water  
is used, the product is conveniently distilled therefrom  
under vacuum. Otherwise the solvent may be evaporated  
from the product as by heating under vacuum on a rotary  
evaporator. Purification of the 2-halotetrafluoroethyl  
15 compound is advantageous to subsequent reactions.

The non-fluorine halogen atom and one fluorine  
atom are then eliminated from the product 2-halo-  
tetrafluoroethyl compound to form the perfluorovinyl  
20 compound. The elimination is suitably conducted by any  
effective means. Preferably a metallic reagent such as  
zinc or magnesium is reacted with the 2-halo-  
-tetrafluoroethyl compound, preferably in a liquid  
medium such as the ones suitable for formation of the  
25 salt. Alternatively, some reactants are sufficiently  
liquid for convenient reaction without solvent. More  
preferably, the 2-halotetrafluoroethyl compound is added  
to a hot, 40°C to 150°C, slurry of (preferably granular)  
30 zinc most preferably in a dry glyme, or other liquid  
media which promotes the elimination reaction. The  
reaction is exothermic and the temperature is regulated  
by the speed of the addition of reactants. Most  
preferably, the halotetrafluoroethyl compound is mixed

-15-

with the metallic reagent in a dry glyme and heated at 85°C to 135°C with stirring until the perfluorovinyl compound is formed, generally several hours, conveniently overnight.

5        After completion of the reaction, any precipitated materials, for example, metal salts are removed by methods within the skill in the art, conveniently by centrifugation. If glyme or a lower boiling solvent is used, the solvent is conveniently 10 removed by rotary evaporation and the product is preferably purified by vacuum distillation. Otherwise, purification means within the skill in the art, such as fractional distillation are used.

15        Such preparations yield compounds of the present invention having at least two perfluorovinyl groups. The perfluorovinyl groups are thermally reacted to form perfluorocyclobutane rings which link the 20 compounds into polymers.

25        Polymers produced from the preferred monomers, advantageously have a formula represented by Formula II:

30        where R, X, and m, are defined above, Q is a perfluorocyclobutane group; and n is an integer representing the number of repeating units, which is preferably from 2 to 100,000. More preferably from 2 to 10,000, most preferably from 3 to 5,000. More preferably m is one or two. Formula II is generalized;

when m is greater than one, some of the -X-Q- structures represent branching and/or crosslinking.

The monomers are heated to a temperature and for a time sufficient to form perfluorocyclobutane rings. Temperatures suitable for forming 5 perfluorocyclobutane rings differ with the structure of the monomer. In general, temperatures above about 40°C are suitable for formation of perfluorocyclobutane rings, preferably the temperature is above about 50°C, 10 more preferably above about 100°C, because these temperatures result in formation of the rings at successively faster rates. Temperatures above about 450°C are preferably avoided because perfluorocyclobutane groups are generally thermally 15 unstable above such temperatures. Most preferably a temperature of from 105°C to 350°C, most preferably from 105°C to 250°C, is used to produce the perfluorocyclobutane rings at a convenient rate. Within 20 that range, a temperature of from 100° to 230° is generally most preferred for cyclization of perfluorovinyl aromatic or aliphatic ethers or sulfides, while a temperature of from 50°C to 80°C is needed to 25 form perfluorocyclobutane groups when the perfluorovinyl group is attached directly to an aromatic ring. In the case of perfluoroalkylperfluorovinyl groups, however, temperature at least about 300°C, preferably at least about 350°C, are generally required.

30 Preferably, especially when the perfluorovinyl compounds are capable of addition polymerization, conditions conducive to free radical polymerization, for example, presence of oxygen, ozone, peroxygen compounds and other free radical generating compounds are avoided

so that the perfluorovinyl groups will dimerize into perfluorocyclobutane groups rather than undergoing addition polymerization. Compounds known in the art for stabilization against free radical polymerization are alternatively used. Similarly, especially when the 5 perfluorovinyl groups are capable of addition polymerization in the presence of anions or cations, compounds which supply such anions or cations are avoided. For instance, fluoride ions (for example from carbonyl fluorides) chloride, hydroxide and phenoxide 10 are preferably avoided. To avoid such compounds as carbonyl fluorides, oxidative conditions such as presence of oxygen, hypochlorite, dichromate, and permanganate are preferably avoided because perfluorovinyl groups are known to oxidize to form 15 carbonyl fluorides.

Monomers or admixtures thereof are suitably neat or, optionally, in admixture with other materials 20 such as in solution, in emulsion, in dispersions or in any other form in which monomer molecules can be contacted with one another to form a polymer. Liquid admixtures are advantageous for maintaining contact 25 between monomer molecules such that higher molecular weight polymers are formed. This is particularly useful when linear thermoplastic polymers are the products. Neat polymerization is preferred when the monomers or 30 prepolymers are formed in the final desired shape of the polymer article. This is especially true when monomers having more than two perfluorovinyl groups are used in whole or in part to form crosslinked, thermoset materials. Neat polymerizations or oligomerizations are

-18-

also generally preferred to form relatively low molecular weight fluid products.

Suitable solvents are those which are inert to the conditions encountered in the polymerization reaction and include, for example, xylene, mesitylene, 5 and perfluorotetradecahydrophenanthrene (MULTIFLUOR™ APF 215 commercially available from Air Products Corp.). At atmospheric pressure preferred solvents are those which attain temperatures of 170°C to 250°C such as 10 dichlorobenzene, trichlorobenzene, diphenyl oxide and perfluorotetradecahydrophenanthrene. Although solvents such as 1,2-dichlorobenzene and 1,2,4-trichlorobenzene give less satisfactory results such as discoloration of the finished polymer, they are suitably used when their 15 disadvantages are tolerable in a final product. When a solvent is used the concentration of monomers in solvent is advantageously from 0.1 molar to 99.9 M weight percents preferably, from 10 to 90 percent by weight 20 monomer.

Polymerization or dimerization suitably takes place at any pressure. Pressures are generally chosen such that the monomers and any solvents and/or 25 dispersing media remain liquid at the temperatures used for polymerization. When the monomers or other materials evaporate at temperatures used, then it is generally preferable to maintain a pressure at least sufficient to maintain the materials liquid.

30

Additional detail regarding these polymerization processes are found in copending U.S.

- 19 -

Patent Application Serial No. 364,667 filed  
June 9, 1989.

All gas chromatography/mass spectrometry (GC/MS) analyses of monomers and intermediates are 5 performed on a Finnigan 1020 GC/MS using a 30 meter RSL-150 fused silica capillary column. All gas chromatography/mass spectrometry (GC/MS) analyses of fluid polymer samples are performed on a Finnigan 10 4500 GC/MS using a 60 meter DB-1 fused silica capillary column, with the GC program run at 290°C isothermal. Mass to charge (M/e) ratios and percentage of peak height relative to tallest (parent) peak are given. Liquid chromatography/mass spectrometry (LC/MS) is 15 performed on a Finnigan 4500 mass spectrometer using acetonitrile - water eluent and a moving belt LC/MS interface.

Dynamic Mechanical Spectroscopy (DMS) 20 measurements are performed on a Rheometrics RDS-7700 rheometer in torsional rectangular geometry mode using 60mm x 12mm x 3mm samples at 0.05 percent strain and 1 Hz. Differential scanning calorimetry (DSC) is 25 performed on a Perkin Elmer 7000 thermal analysis system scanning from ambient temperature to 350°C at 20°C per minute.

Dielectric constant and dissipation factor 30 measurements are conducted according to the procedures of ASTM D150-87. Tensile strength and modulus and percent elongation were measured on an Instron model 1125 according to the procedures of ASTM D-882-83.

Gel Permeation Chromatography (GPC) is performed on a Waters 720 GPC instrument using a

-20-

methylene chloride eluent and a series of Micro-styragel™ columns of 10,000, 1,000, 500 and 100 angstrom pore sizes. Reported values are standardized against polystyrene.

5 Granular zinc is activated by washing in 0.1 N hydrochloric acid (HCl) followed by drying in a vacuum oven at 0.5 mmHg (66.5 Pa) and 140°C for 10 hours.

10 15 Infrared (IR) spectra are measured on a Beckmann Microlab 600 model spectrophotometer. Nuclear Magnetic Resonance (NMR) spectra are measured on a Varian EM360 spectrometer using <sup>19</sup>F (fluorine 19) or <sup>1</sup>H (hydrogen) mode.

15 EXAMPLE 1: PREPARATION AND BULK POLYMERIZATION OF 4,4'-BIS(TRIFLUOROVINYLOXY)BIPHENYL

20 25 Dimethyl sulfoxide (DMSO) (1800 mL) was placed in a 5-liter 5-necked flask fitted with a mechanical stirrer, a Dean-Stark phase separating trap topped with a nitrogen padded reflux condenser, and a thermocouple attached to a temperature controller. The solvent was stirred and purged of oxygen by blowing in nitrogen through a dip-tube placed below the surface of the liquid while 4,4'-dihydroxybiphenyl (454 g, 2.44 mole) was added to the flask.

30 The system was stirred and purged for 20 minutes, then potassium hydroxide (85 percent pellets) (322 g, 4.88 mole) was added slowly. The stirred mixture was then heated to 120°C. The temperature was held at 120°C for 1.5 hours, then the heat was turned off and the mixture was allowed to cool to room temperature. Toluene (600 mL) which has been thoroughly

purged with nitrogen was added to the solution and the resulting mixture was heated to reflux (135°C). Water was azeotropically removed from the reactor through the Dean-Stark trap for a total of 4 days, cooling the reactor once after 24 hours to allow for salt formation 5 to be broken up by opening the flask under a nitrogen sweep and scraping the sides with a spatula. After 4 days, the Dean-Stark trap was removed and replaced with a Soxhlet extractor containing anhydrous sodium sulfate. The toluene was then refluxed through the 10 Soxhlet extractor for 7 hours to dry the toluene. After 7 hours, the Soxhlet was replaced with a Dean-Stark trap, and toluene (300 mL) was removed from the reactor by simple distillation. The reaction mixture was then 15 cooled to 30°C in an ice water bath and 1,2-dibromotetrafluoroethane (1300 g, 5.00 mole) was added slowly dropwise over three hours at a rate that maintained a reactor temperature of 35°±2°C. When the addition was completed the reaction temperature was 20 allowed to stabilize (not increasing in temperature when the ice bath was removed) and then a heating mantle was applied to the flask. The reactor was heated to 50°C for 8 hours, then allowed to cool to room temperature with constant stirring. The crude reaction mixture was 25 filtered to remove the potassium bromide salts, and the precipitate was washed with acetone. The filtrates were combined and thoroughly evaporated to remove acetone, DMSO and residual toluene. The solid residue was subjected to a 2-liter Kugelrohr bulb-to-bulb 30 distillation to provide the crude product. This material was dissolved in 750 mL of methylene chloride and was washed first with mild aqueous potassium bicarbonate (500 mL, approximately. 0.2 M), then with mild aqueous hydrochloric acid (HCl) (500 mL,

5 approximately 0.05 M), then twice with distilled water (500 mL each). After complete phase separation the product layer was removed and evaporated, and the residue was fractionally distilled (138°C to 148°C, 0.35 mmHg (46.5 Pa)) to provide 1031.1 g (1.90 mole, 77.9 percent yield) of 4,4'-bis(2-bromotetrafluoroethoxy)biphenyl, melting point 71°C to 73°C. The Infrared (IR) spectra of the product had the following peaks (cm<sup>-1</sup>): 1601, 1492 (indicating an aromatic double bond); 1199-1107 (indicating carbon-oxygen and carbon 10 fluorine bonds); 842, 788 (indicating aromatic character). The gas chromatograph/mass spectrometer (GC/MS) indicates peaks at the following mass to charge ratios: (m/e) = 545 (29.8%); 543 (48.9%); 541 (23.8%); 365 (48.7%); 363 (50.9%); 337 (30.3%); 335 (34.7%); 168 (33.7%); 156 (78.3%); 140 (36.7%); 139 (90.1%); 129 (37.4%); 128 (100.0%); 127 (33.2%); 102 (32.9%); 76 (41.1%); 63 (34.3%), consistent with a product of 15 4,4'-bis(2-bromotetrafluoroethoxy)biphenyl.

20        Bromine was eliminated from this product by the  
following procedure:

25 Into a 1-liter 5-necked flask equipped with a mechanical stirrer, a thermocouple attached to a temperature controller, a powder addition funnel and a reflux condenser, was placed freshly distilled diglyme (200 mL) and fresh zinc powder (36.0 g, 0.55 mole).

30 The mixture was stirred and heated to 130°C. Powdered 4,4'-bis(2-bromotetrafluoroethoxy)biphenyl (100 g, 0.184 mole) was added very slowly via the powder addition funnel over 3.5 hours. The mixture was then stirred mechanically at 115°C for 1 hour, after which,

-23-

heating was turned off and the mixture was allowed to cool to room temperature. The solution was centrifuged to remove the zinc salts. Then the liquid was decanted, and the zinc salts were washed with acetone and centrifuged again. The liquid portions were combined and evaporated thoroughly, and the residue was dissolved in methylene chloride and washed with 0.05 M hydrochloric acid. The methylene chloride solution was evaporated to provide 62.45 g (0.180 mole) of 4,4'-bis(trifluorovinyloxy)biphenyl of 94.5 percent 5 purity in 98 percent yield.

10 The product was then recrystallized in an ethanol/water mixture to give product of 99.8 percent 15 purity in greater than 70 percent recovery, melting point 44°C to 46°C.

15 The IR spectrum shows peaks at (cm<sup>-1</sup>): 1833 (indicative of a perfluorovinyl group); 1601, 1491 20 (indicative of an aromatic double bond); 1231, 1196-1132 (indicative of carbon-oxygen and carbon-fluorine bonds respectively); 818 (indicative of aromaticity).

25 The GC/MS spectrum had the following peaks:  
m/e: 346 (31.3%); 153 (13.8%); 152 (100.0%);  
151 (27.0%); 150 (11.7%); 76 (14.9%); 63 (14.9%).

30 Differential scanning calorimetry (DSC) analysis of the 4,4'-bis(trifluorovinyloxy)biphenyl monomer (20°C to 360°C at 20°C/minute) indicated a sharp endotherm of melting beginning at 45°C, followed by a broad exotherm beginning at about 170°C, interpreted as corresponding to the heat of cyclization of the

-24-

trifluorovinyl groups to form hexafluorocyclobutane rings.

The monomer, 4,4'-bis(trifluorovinyloxy)-biphenyl, (15.0g, 0.043 mole) was placed in a nitrogen purged 100 mL round bottom flask and polymerized by heating at 210°C for 2 hours without stirring. After cooling, a small sample was removed for analysis by differential scanning calorimetry (DSC). The sample showed a small crystalline melt with a peak at 60°C, followed by a broad exotherm beginning at about 200°C. The bulk sample was heated again at 235°C for an additional 3 hours. Again a sample was removed and analyzed by DSC. The analysis indicated a very small crystalline melt with a peak at 60°C, followed by a low intensity exotherm beginning at about 230°C. The bulk sample was heated again to 265°C for 45 minutes. Analysis of this sample indicated no crystalline melt and no exothermic activity up to and including 325°C, with the emergence of an endothermic glass transition (Tg) at 143°C.

EXAMPLE 2: POLYMERIZATION OF 4,4'-BIS(TRIFLUOROVINYLOXY)BIPHENYL IN SOLUTION

The monomer, 4,4'-bis(trifluorovinyloxy)-biphenyl, (60.0g, 0.173 mole) was placed in a 1-liter 3-necked round bottom flask with 75 mL of perfluorotetradecahydrophenanthrene (Multifluor™ APF 215 commercially available from Air Products). The flask was fitted with a mechanical stirrer and a nitrogen padded reflux condenser. After purging the flask thoroughly with nitrogen, the mixture was stirred and heated to reflux. Initially, upon heating the

-25-

5        melted monomer was not miscible with the solvent; but as the temperature rose the two phases became homogeneous. After stirring at reflux for approximately 45 minutes, a polymer phase separated; and, after stirring at reflux for a total of 3 hours, the phase separated polymer became viscous enough to seize the stirring shaft. The cooled polymer was removed from the flask and evaporated under high vacuum (approximately 0.50 mmHg (66.5 Pa)) at about 220°C for 3 hours to remove residual solvent. A portion of this polymer was compression molded at 250°C  
10      to provide a light yellow, transparent flexible plastic film. Another portion was dissolved in tetrahydrofuran and placed in an evaporating dish to make a solvent-cast film. After the solvent was evaporated overnight, a light yellow thin film was peeled from the dish. This sample exhibited excellent flexibility and transparency.  
15

20        An IR spectrograph of the film had the following peaks (cm<sup>-1</sup>): 1601, 1490 (indicating aromatic double bonds); 1302, 1194-1115 (indicating carbon-oxygen and carbon-fluorine bonds), 818 (indicating aromaticity).

25        DSC analysis of this polymer indicated a T<sub>g</sub> transition at 148°C.

30        Dynamic mechanical analysis (DMS) gave a T<sub>g</sub> value of 170°, and gel permeation chromatography (GPC) indicated a weight average molecular weight of 85,000 as standardized against polystyrene.

Dielectric constant and dissipation factor measurements performed on this polymer give the following results:

5

Frequency (kHz)	Dielectric Constant	Dissipation Factor
1.0	2.58	0.0007
10.0	2.57	0.0004
1000.0	2.55	0.0004

10 Examples 1 and 2 illustrated two types of polymerization of 4,4'-bis(trifluorovinyloxy)biphenyl. It was notable that the properties of each were roughly similar, with slightly more discoloration taking place in the bulk polymerization (according to the procedures of Example 1).

15

EXAMPLE 3: PREPARATION AND POLYMERIZATION OF 9,9-BIS(4'-[TRIFLUOROVINYLOXY]PHENYL)FLUORENE

20 Into a 2 liter 5-necked round bottom flask fitted with a mechanical stirrer, Dean-Stark trap topped with a nitrogen padded reflux condenser and a thermocouple attached to a temperature controller, were placed DMSO (650 mL) and toluene (200 mL). While the stirred solution was purged with nitrogen, 9,9-bis(4'-hydroxyphenyl)fluorene (200.0 g, 0.57 mole) was added to the flask. While purging with nitrogen continued, potassium hydroxide (85 percent pellets, 77.5 g, 1.17 mole) was added all at once, and the mixture was 25 heated to 100°C with constant stirring. After two hours, the temperature was increased until the solution began to reflux (130°C). Water was removed by azeotropic distillation for 24 hours. The Dean-Stark trap was replaced by a Soxhlet extractor containing 30

anhydrous sodium sulfate, and the toluene was refluxed through the Soxhlet for 5 hours. A small amount of toluene (60 mL) was then removed by simple distillation. Then the reactor was cooled to 35°C. Addition of 1,2-dibromotetrafluoroethane (315 g, 1.21 mole) via dropping addition funnel was then maintained at a rate that keeps the reaction temperature at 35°C to 38°C. When the addition was completed, the mixture was heated at 50°C for 8 hours, then cooled to room temperature with constant stirring. The mixture was filtered, and the precipitate was washed twice with acetone. The filtrates were combined and evaporated thoroughly. The residue from the evaporation was washed with water to remove residual potassium bromide (KBr). After the residue was air dried for 24 hours, it was purified by column chromatography (on neutral alumina, using hexane eluent) to provide as product, 9,9-bis(4'-[2"-bromo-tetrafluoroethoxy]phenyl)fluorene (331.4g, 0.468 mole, 82 percent yield), melting point 157°C to 158°C.

20

The LC/MS spectrum had peaks at: m/e: 710 (53.0%); 709 (34.0%); 708 (100.0%); 707 (23.3%); 706 (49.8%); 513 (28.4%); 511 (28.5%); 438 (12.8%); 437 (52.4%); 436 (14.7%); 435 (55.8%); 355 (15.7%); 290 (33.9%); 289 (19.5%); 239 (35.9%); 228 (36.2%); 227 (38.9%); 226 (47.3%); 202 (27.7%); 157 (47.2%); 131 (27.6%); 129 (23.1%).

30

The product from the above reaction (18.85g, 0.027 mole) was combined with freshly activated granular zinc (5.00 g, 0.076 mole) in glyme and heated at reflux overnight. After cooling, the reaction mixture was decanted and centrifuged to remove suspended zinc salts. The solvent was removed by vacuum evaporation, and the

-28-

residue was purified by column chromatography on neutral alumina using hexane as an eluent to provide as product 9,9-bis(4'-trifluorovinyloxyphenyl)fluorene (5.55g, 0.011 mole, 40 percent yield), melting point 115°C to 116°C.

5

The LC/MS spectrum had peaks at: m/e: 511 (29.3%); 510 (91.9%); 337 (37.2%); 316 (16.1%); 315 (19.7%); 313 (12.8%); 241 (15.5%); 240 (52.8%); 239 (100.0%); 237 (15.6%); 207 (14.1%); 158 (28.7%); 157 (53.1%); 155 (14.4%); 150 (28.8%); 145 (18.3%); 144 (16.5%); 120 (15.1%).

10  
15  
20  
25

Into a 50 mL round bottom flask fitted with a nitrogen padded reflux condenser, mechanical stirrer and a thermocouple attached to a temperature controller were placed 9,9-bis(4'-trifluorovinyloxyphenyl)fluorene (3.0 g, 0.0059 mole) and diphenyloxide (5.0 mL). The mixture was stirred and heated to reflux (255°C) for 22 hours. The diphenyloxide (DPO) solvent was evaporated under high vacuum on a 100 milliliter Kugelrohr bulb to bulb apparatus (0.03 mm, 165°C) to provide the polymer product, which was dissolved in methylene chloride and cast into a thin film.

30

Gel permeation chromatography analysis of the polymer indicated a weight average molecular weight of 135,000 as standardized against polystyrene.

30

DSC analysis indicated a T<sub>g</sub> transition at 224°C.

Example 3 illustrates preparation and polymerization of 9,9-bis(4,4'-trifluorovinyl-oxyphenyl)fluorene. It was notable that the resulting

-29-

polymer, which was polymerized in DPO, attained a high molecular weight and formed a solvent cast film with good physical properties such as flexibility.

5        EXAMPLES 4-9: PREPARATION AND POLYMERIZATION OF A  
VARIETY OF PERFLUOROCYCLOBUTANE RING-CONTAINING POLYMERS

10       The procedure outlined in Example 3 was repeated for each of the indicated starting materials, except for the changes indicated in Table I and  
10       adjustments in amounts to maintain the stoichiometry of Example 3, to produce the indicated monomers of the structure:



wherein R is given in Table I

20

25

30

-30-

Table I: Preparation of Monomers

EX. NO.	STARTING MATERIAL	R	Changes in procedure
4	Resorcinol	1,3-Phenylene	Tetraglyme is used in second step. Product is distilled directly from reaction mixture under vacuum. *3-(1',1',2',2'-tetrafluoroethoxy)-trifluorovinyl oxybenzene and 1,3-bis(1',1',2',2',2'-tetrafluoroethoxy)benzene are isolated as by products and identified by GC/MS spectra consistent with those compounds.
5	4,4'-dihydroxy- biphenyl	4,4'-Biphenyl	See Example 1
6	4,4'-thiodiphenol	4,4'-Thiodiphenyl	Tetraglyme is used in second step, removed by diluting with methylene chloride and washing with water.
7	Bisphenol A	Isopropyl-2,2'- diphenylene	
8	Hexafluorobisphenol A (bisphenol AF)	Hexafluoroisopropyl- 2,2-diphenylene	
9	9,9-bis(4'- hydroxyphenyl)fluorene	9,9-bis(4'- phenylene)fluorene	See Example 3

-31-

The data in Table I shows that a variety of perfluorovinyl monomers are prepared by processes within the scope of the present invention.

The procedure outlined in Example 2 was 5 repeated for each of the monomers in Table I, except for the changes in procedure indicated in Table II to produce polymers from the indicated monomers. The properties of these polymers are given in Table II.

10

15

20

25

30

-32-

Table II: Properties of Thermoplastic Polymers

Ex.	R	T <sub>g</sub> (°C)	Dielectric Constant 10 kHz	Dissipation Factor 10 kHz	Wt. Ave. Molecular Weight
4	1,3-Phenylene	32°	2.41	--	41,400
5	4,4'-Biphenyl	170°	2.57	0.0004	85,000
6	4,4'-Thiodiphenyl	78°	2.62	0.0005	42,500
7	Isopropyl-2,2'- diphenylene	98°	--	--	50,700
8	Hexafluoroisopropyl-2,2'- diphenylene	125°	--	--	23,500
9	9,9-bis(4'- phenylene)fluorene (prepared in diphenyloxide)	224°	--	--	135,000

The data in Table II shows that a variety of perfluorocyclobutane ring-containing polymers were prepared by processes within the scope of the present invention.

5 EXAMPLE 10: PREPARATION OF 1,1,1-TRIS(4'-TRIFLUOROVINYLOXYPHENYL)ETHANE AND BULK POLYMERIZATION THEREOF WITH 4,4'BIS(TRIFLUOROVINYLOXY) BIPHENYL

10 A 1-liter 5-necked round bottom flask was fitted with a mechanical stirrer, a Dean-Stark trap topped with a nitrogen padded reflux condenser, and a thermocouple attached to a temperature controller. A mixture of DMSO (450 mL), toluene (150 mL), and 15 1,1,1-tris(4'-hydroxyphenyl)ethane (55.1 g, 0.18 mole) was added to the flask under nitrogen purge. After stirring for 15 minutes under a vigorous nitrogen purge, potassium hydroxide (85 percent pellets, 80.0 g, 1.2 mole) was slowly added to the reaction flask. The 20 mixture was then stirred at reflux for 48 hours with azeotropic removal of water. The resulting suspension was cooled to 35°C in an ice bath and 1,2-dibromotetrafluoroethane (155 g, 0.60 mole) was added at a rate that maintained a temperature of 30°C to 35°C. When the 25 addition was completed, the mixture was heated to 50°C with continuous stirring for 3 hours. After filtration, the solvents were removed by heating under vacuum on a rotary evaporator. The brown residue was purified by 30 column chromatography on neutral alumina using hexane as eluent to provide as product 1,1,1-tris(4'-[2"-bromo-tetrafluoroethoxy]phenyl)ethane (18.3 g, 0.022 mole, 12 percent yield).

-34-

Identity of the product was confirmed by a GC/MS spectrum, the following peaks: m/e: parent ions m/e 840-842-844-846 (ratio 1:3:3:1) too heavy to detect. Structure determined from fragmentation: 573 (32.3%); 571 (58.3%); 569 (31.5%) [indicating parent 5 - PhOCF<sub>2</sub>CF<sub>2</sub>Br]. 299 (58.1%); 297 (52.7%); 279 (32.3%); 228 (43.5%); 227 (31.5%); 226 (36.0%); 215 (59.5%); 181 (82.1%); 179 (100.0%); 165 (50.3%); 152 (43.7%); 131 (47.1%); 129 (50.4%); 100 (38.8%).

10        Into a 500 mL 5-necked flask fitted with a mechanical stirrer, a reflux condenser, and a thermocouple attached to a temperature controller was placed freshly activated granular zinc (4.3 g, 0.066 mole) and 25 mL dry diglyme. This mixture was 15 stirred and heated to 110°C under nitrogen while the product from the above reaction (18.0 g, 0.021 mole) was dissolved in 21 mL diglyme and added dropwise. The resulting mixture was stirred at 115°C for 3 hours, then 20 cooled and filtered. The filtrate was evaporated at 60°C under vacuum to remove the diglyme, and the residue was purified by column chromatography on neutral alumina using hexane as eluent to provide the product 25 1,1,1-tris(4'-trifluorovinyloxyphenyl)ethane (9.98 g, 0.018 mole, 87 percent yield).

30        The GC/MS spectrum has the following peaks: m/e: 546 (3.2%); 531 (44.0%); 434 (17.9%); 373 (24.4%); 276 (16.9%); 240 (28.1%); 239 (73.9%); 199 (19.3%); 178 (100.0%); 177 (17.8%); 176 (25.4%); 163 (17.3%); 152 (31.9%); 151 (17.8%); 127 (20.3%); 126 (28.7%); 120 (39.1%); 119 (70.3%); 118 (25.6%); 113 (27.3%); 107 (18.8%); 102 (31.7%); 77 (15.9%); 76 (29.5%).

This example illustrates preparation of a trifunctional monomer, 1,1,1-tris(4'-trifluorovinyloxyphenyl)ethane. This monomer was useful alone or mixed with a bifunctional monomer to produce a crosslinked perfluorocyclobutane polymer.

5

A mixture of 4,4'-bis(trifluorovinyloxy)-biphenyl (as prepared in Example 1) (4.50 g, 0.013 mole) and the 1,1,1-tris(4'-trifluorovinyloxyphenyl)ethane (0.79 g, 0.0014 mole) were combined in a 100 mL single-necked round-bottomed flask topped with a nitrogen padded reflux condenser. The flask was purged thoroughly with nitrogen, and the mixture was heated without stirring. After reaching a temperature of 200°C, the mixture sets into a rigid plastic within 15 minutes. This material was then cured an additional 40 minutes at 220°C; then the heat was removed. The resulting plastic was rigid, inflexible and does not dissolve in tetrahydrofuran (THF) or methylene chloride, but swells into a gel in these solvents.

DSC analysis (25°C to 350°C, 20°C/minute) of this polymer sample showed a slight endothermic event at 125°C followed by a broad exotherm beginning at about 210°C, indicative of an incompletely cured polymer. After this sample was cured during the first DSC scan, a second scan was run which clearly indicates a Tg transition at 151°C and no subsequent exothermic activity at higher temperatures.

Example 10 illustrates preparation of 1,1,1-tris(4'-trifluorovinyloxyphenyl)ethane and copolymerizaton thereof 4,4'-bis(trifluorovinyloxy)--biphenyl therewith. The resulting polymer was stiff and

brittle, as well as insoluble, compared to the thermoplastic of Example 2, prepared from 4,4'-bis(trifluorovinyloxy) biphenyl alone, which was flexible and soluble in THF and methylene chloride.

5 EXAMPLE 11: BULK POLYMERIZATION OF 4,4'-  
BIS(TRIFLUOROVINYLOXY)BIPHENYL WITH SUBSEQUENT ADDITION  
OF 1,1,1-TRIS(4'-TRIFLUOROVINYLOXYPHENYL)ETHANE

Monomer 4,4'-bis(trifluorovinyloxy)biphenyl  
10 (16.2 g, 0.047 mole) was placed in a 500 mL round bottom flask along with a magnetic stirring bar. A nitrogen padded reflux condenser was placed on the flask, and the monomer was heated at 200°C to 205°C with stirring for 20 minutes, to form a low molecular weight polymer  
15 resembling a thick fluid at 200°C. The fluid was allowed to cool to room temperature where it sets into a brittle glass. The glass was dissolved in methylene chloride and 1,1,1-tris(4'-trifluorovinyloxyphenyl)ethane (0.51 g, 0.00094 mole)  
20 was added to the solution. The methylene chloride was evaporated and the residue was dried and devolatilized on a Kugelrohr bulb to bulb apparatus at 120°C to 140°C and 0.20 mmHg (26.6 Pa) pressure. While still hot, the  
25 fluid mixture was poured into a mold and cured on a hot press at 250°C and 20,000 psi for one hour. The mold was removed from the press and cooled. A coupon was removed from the mold. The coupon was a strong and flexible plastic, and did not dissolve in THF but swells  
30 into a gel therein.

DSC analysis of this crosslinked polymer sample indicated a Tg value of 149°C, with no subsequent thermal activity up to and including 350°C.

Example 11 illustrates polymerizaton of 4,4'-bis(trifluorovinyloxy)biphenyl with subsequent addition of 1,1,1-tris(4'-trifluorovinyloxyphenyl)-ethane. It was notable that crosslinked polymers were prepared either by copolymerizing difunctional and multi-functional monomers, as in Example 10, or by combining a multifunctional monomer with a low molecular weight polymer containing trifluorovinyl end groups as in Example 11.

EXAMPLE 12: PREPARATION OF 1,4-BIS(TRIFLUOROVINYL)BENZENE AND BULK POLYMERIZATION THEREOF

A 5-liter 3-necked round bottom flask was fitted with a mechanical stirrer, a nitrogen padded reflux condenser and a rubber septum. Glyme (100 mL) and activated zinc granules (11.50 g, 0.18 mole) were added to the flask along with a magnetic stirring bar. The flask was then purged with nitrogen for 15 minutes, after which time iodotrifluoroethylene (20.3 g, 0.098 mole) was added slowly via syringe through the septum. After 20 minutes of stirring the mixture began to turn brown and get warm. After 2 hours a white precipitate began to form. After stirring was continued without heat for 4 hours, the flask was opened under a slow nitrogen purge and 1,4-diiodobenzene (16.0 g, 0.0485 mole) was added along with palladium tetrakis(triphenylphosphine) (0.57 g, 0.00049 mole). The mixture was stirred overnight, resulting in the

-38-

formation of a large amount of suspended solid. The reaction was stirred an additional 24 hours, after which it was filtered, and the precipitate was washed with hexane (3 times with 50 mL each wash). The filtrates were combined and evaporated at 30°C on a rotary evaporator to provide a residue which was purified by 5 column chromatography (neutral alumina, hexane eluent) to give 7.50g of  $\text{CF}_2=\text{CF-Ph-CF=CF}_2$  as product (0.0315 mole, 65 percent yield). This product was analysed by GC/MS and gives the following spectrum: m/e: 10 238 (100%); 188 (12.0%); 187 (46.4%); 169 (92.0%); 138 (18.8%); 99 (16.3%); 81 (12.3%); 69 (30.1%). The material was found to be air sensitive, fuming acid gasses if left exposed to oxygen.

15        This example illustrates preparation of an aromatic monomer having two perfluorovinyl groups directly attached to the aromatic ring and illustrates the use of iodotrifluoroethylene in preparation of a 20 monomer. This preparation proceeds via a one pot synthesis to give good yields of the monomer.

It was noted that when a sample of this material was stored for 10 hours or more in contact with 25 air that a highly mobile gel was formed along with the evolution of acid fumes. This observation was believed to be indicative of formation of acyl fluorides and fluoride ions, and of addition polymerization (rather than cyclization) catalyzed by the fluoride ion. The 30 result of such storage in contact with air differs from the following product in that only a very low molecular weight gel was formed, with a high degree of crosslinking taking place in the gel matrix.

-39-

Monomer 1,4-bis(trifluorovinyl)benzene (1.00 g, 0.0042 mole) was placed in a 100 mL round bottom flask with a magnetic stir bar and purged with nitrogen. The neat monomer was heated to about 80°C with slow stirring. In 10 minutes the monomer sets into a hard 5 glassy polymer which was not soluble in THF or methylene chloride, but which turned brown and fumes acid gasses when left exposed to air overnight. This observation suggested that a low molecular weight polymer was formed 10 and contained unreacted trifluorovinyl groups which were still air sensitive.

Example 12 illustrates polymerization of an aromatic monomer having two perfluorovinyl groups 15 directly attached to the aromatic ring, which polymerization proceeds in a very short time and without the need of solvents.

EXAMPLE 13; SOLUTION POLYMERIZATION OF 1,4-  
20 BIS(TRIFLUOROVINYL)BENZENE

Monomer 1,4-bis(trifluorovinyl)benzene (1.00 g, 0.0042 mole) was combined in a 100 mL round bottom flask with 2.0 g of perfluorotetradecahydrophenanthrene 25 (Multifluor™ APF-215 commercially available from Air Products) and a magnetic stirrer. The flask was topped with a nitrogen padded reflux condenser. When the mixture was purged with nitrogen, it was heated to 30 reflux with stirring. After 10 minutes, a crystalline precipitate was formed. This precipitate was isolated by filtration followed by vacuum drying.

The material was insoluble in THF or methylene chloride. A powder was formed by crushing the polymer

-40-

precipitate in a mortar and pestle. Analysis of the powder by DSC indicated two small exothermic events, one at 180°C to 240°C, the other at 320°C to 380°C leading into decomposition.

5 Example 13 illustrates solution polymerization of an aromatic monomer having two perfluorovinyl groups directly attached to the aromatic ring. This polymerization proceeds very quickly at higher 10 temperatures and in the presence of inert solvents such as that used above.

EXAMPLE 14; PREPARATION AND POLYMERIZATION OF 4,4' - BIS(TRIFLUOROVINYL)BIPHENYL:

15 A 1 liter 5-necked round bottom flask was fitted with a mechanical stirrer, a nitrogen padded reflux condenser and a rubber septum. Dry glyme (300 mL) and activated zinc granules (50.8 g, 0.395 mole) were added to the flask as it was purged thoroughly with nitrogen. Then iodotrifluoroethylene (100.0 g, 0.48 mole) was added to the flask all at once, and the mixture was stirred continuously under nitrogen for 5 hours. 4,4'-Diiiodobiphenyl (97.0 g, 0.24 mole) 20 was added to the flask along with nitrogen purged dimethylformamide (DMF) (300 mL) and palladium 25 tetrakis(triphenylphosphine) (4.35 g, 0.0038 mole). The mixture was stirred at room temperature.

30 After 24 hours, a GC/MS of the mixture was used to identify of all the reaction components. After 72 hours, the reaction seems to stop proceeding while excess diiodobiphenyl remains; another batch of iodotrifluoroethylene (25.0 g, 0.12 mole) was reacted

-41-

with zinc in THF and added to the reaction mixture along with 1.0 g of palladium tetrakis(triphenylphosphine) catalyst. The reaction was stirred an additional 12 hours, then was removed and evaporated to dryness under high vacuum on a rotary evaporator. Residue from evaporation was added to a 3-fold volumetric excess of water. A heavy precipitate was formed which was filtered and air dried on a vacuum funnel. The precipitate was dissolved in THF and filtered. The resulting filtrate was coated on silica gel by adding the silica gel to the THF solution and evaporating to dryness. This silica gel was then eluted on a short silica gel column using hexane as eluent to remove the colored material from the product. A fine white crystalline material remained after evaporation of the hexane. This crystalline material was then chromatographed again carefully on an alumina column using hexane as an eluent. The first band to elute from the column was the desired monomer product  $CF_2=CF-Ph-Ph-CF=CF_2$ . A total of 44.2 g of product was recovered (58.7 percent yield).

The crystalline product has a melting point of 83°C to 84.5°C.

25

Analysis by GC/MS gave the following mass spectral data for this product: m/e: 314 (100.0%); 263 (13.4%); 243 (14.9%); 69 (13.0%).

30

DSC analysis of this monomer shows a sharp endotherm at about 82°C followed closely by a broad exotherm corresponding to cyclization of the trifluorovinyl groups beginning at about 98°C. A second exothermic event begins at about 300°C leading

into decomposition at greater than 400°C. The monomer was also oxidatively unstable, as indicated by turning brown and releasing acid fumes when allowed to stand in air.

5 Example 14 illustrates preparation of another aromatic monomer having two perfluorovinyl groups directly attached to the aromatic ring. Because of the crystalline nature of this product, a gel was not formed on standing, although oxidative decomposition does 10 appear to evolve acid gasses at a somewhat slower rate than the product of Example 12.

15 A sample of the 4,4'-bis(trifluorovinyl)-biphenyl (1.6 g, 0.005 mole) and fresh anhydrous DMF (5.0 mL) were added to a 100 mL single-necked round bottom flask with a thermometer port along with a magnetic stirrer. The flask was topped with a nitrogen padded reflux condenser and stirring was begun as 20 nitrogen was allowed to pass out of the thermometer port. After 5 minutes of nitrogen purge, a thermocouple was placed in the thermometer port and heating was begun. The solution was heated to 40°C for 4 hours with no apparent reaction. The temperature was then raised 25 in 10°C increments, holding each new temperature for at least 45 minutes before proceeding to the next higher temperature. After the mixture was stirred at 130°C for 2 hours with no apparent change, the temperature was raised to 135°C and left to stir overnight. The next 30 morning the mixture was somewhat darker and noticeably higher in viscosity. The temperature was then raised to 140°C for 9 hours, after which the mixture became very thick, at which time heating and stirring were stopped. A sample of the viscous liquid was removed and

-43-

evaporated to dryness under vacuum, leaving a brittle crystalline powder. This powder dissolved in methylene chloride but does not filter through a 5 micron filter. Only a few drops of filtrate were recovered, and this filtrate was analyzed by gel permeation chromatography 5 as standardized against polystyrene. As recovered by this method, the soluble portion of the polymer had a weight average molecular weight of 41,600.

DSC analysis of the crystalline polymer showed 10 no thermal activity up to and including 400°C, with apparent decomposition beginning at about 420°C. All of the polymer samples prepared from this monomer were still air sensitive, as was evidenced by fuming of acid 15 gasses after standing in air.

Example 14 illustrates polymerization of an aromatic monomer having two perfluorovinyl groups directly attached to the aromatic ring. This example 20 also illustrates that careful temperature control may be employed to control the rate and extent of polymerization.

**EXAMPLE 15: PREPARATION OF A FLUID POLYMER OF 1,3-  
25 BIS(TRIFLUOROVINYLOXY)BENZENE AND 3-TRIFLUOROVINYLOXY-  
1',1',1'-TRIFLUOROTOLUENE**

To synthesize m-trifluorovinyloxy-1',1',1'-trifluorotoluene, DMSO (400 mL), toluene (140 mL), and 30 3-trifluoromethylphenol (81.0 g, 0.50 mole) were placed in a 1-liter 3-necked flask equipped with a mechanical stirrer, a Dean-Stark trap and a thermocouple attached to a temperature controller. The stirred solution was purged of oxygen by placing a dip tube below the surface

-44-

of the solution and allowing nitrogen to be blown into the solution for 15 minutes. Potassium hydroxide (85 percent pellets, 33.7 g, 0.51 mole) was added to the flask all at once, and a line to supply nitrogen was attached to a reflux condenser which was placed on top 5 of the Dean-Stark trap. The mixture was then heated to 145°C and water was removed azeotropically. When water ceases to collect in the Dean-Stark trap, the 10 temperature of the reaction was increased to 155°C and 100 mL of toluene was removed by distillation, leaving a reaction mixture in the flask.

The reaction mixture was cooled to room temperature, and 1,2-dibromotetrafluoroethane (132.0 g, 0.51 mole) was added slowly using a dropping addition 15 funnel. The mixture was heated to 55°C for 5 hours, then allowed to cool to room temperature. After the suspended solids have settled, the liquid was decanted away from the precipitate and was retained as a mixture 20 of product in DMSO, which was added to a 3 times volumetric excess of water in a separatory funnel and shaken vigorously. The product formed a separate, lower layer at the bottom of the funnel and was removed. This crude product (lower layer) was washed again with 500 mL 25 of water. After drying the washed lower layer over anhydrous magnesium sulfate, the crude product was fractionally distilled. The product, m-(2-bromotetra- 30 fluoroethoxy)-1',1',1'-trifluorotoluene (169°C to 171°C, 150 mmHg (19950 Pa)) gives the following mass spectral data: m/e: 342 (20.1%); 340 (19.8%); 323 (7.9 %); 321 (7.2 %); 211 (25.6 %); 145 (100.0%).

The product of the above reaction (56.0g, 0.164 mole) was combined with granular zinc (12.0g,

-45-

0.18 mole) in dry tetraglyme and stirred at 115°C for 6 hours to form a reaction mixture. The mixture was cooled to room temperature, and a distillation head was placed on the reaction flask. The product was then distilled directly out of the crude reaction mixture (108°C to 110°C, 150 mmHg (19950 Pa)) to give 40.5 g of the product, m-trifluorovinyloxy-1',1',1'-trifluorotoluene, which was 78 percent pure by GC analysis, with the remainder of the product being the by-product m-(1,1,2,2,-tetrafluoroethoxy)-1',1',1'-trifluorotoluene.

10

The product gave the following mass spectral data: m/e: 242 (52.3%); 223 (12.3%); 195 (14.2%); 145 (100%); 125 (18.3%); 95 (30.6%).

15

A mixture was prepared from 1.25 mL of 1,3-bis(trifluorovinyloxy)benzene (as prepared in Example 4) and 8.75 mL of 3-trifluorovinyloxy-1',1',1'-trifluorotoluene to make a total of 10 mL. This mixture was placed in a 50 mL round bottom flask fitted with a nitrogen padded reflux condenser and was refluxed under nitrogen for 20 hours.

25

The resulting product was analyzed by GC/MS and found to be a mixture of hexafluorocyclobutane products whose major components were 1,2-bis(3'-trifluoromethylphenoxy) hexafluorocyclobutane and 1,3-bis(2'-[3"-trifluoromethylphenoxy]hexafluorocyclobutyl)phenyl ether (having two perfluorocyclobutane rings), with a trace amount of 1,2-bis(3'-[2"-(3"-trifluoromethylphenoxy)hexafluorocyclobutyloxy]phenyl) hexafluorocyclobutyl ether.

30

(having three perfluorocyclobutane rings). By vacuum distillation two fractions were collected.

5 The first fraction contained primarily mono-perfluorocyclobutane material consisting of two isomers (cis and trans 1,2-substituted hexafluorocyclobutane) with similar mass spectra (given for one isomer only): m/e: 484 (20.2%); 465 (12.9%); 273 (29.2%); 242 (30.1%); 207 (11.2%); 195 (13.0%); 145 (100.0%).

10 The second fraction contained predominantly di-perfluorocyclobutane material, consisting mainly of three isomers (cis-cis, cis-trans, and trans-trans) of 1,2-substituted hexafluorocyclobutanes, and small amounts of four isomers of a product containing one 15 1,2-substituted hexafluorocyclobutane ring and one 1,3-substituted hexafluorocyclobutane ring (cis-1,2 cis-1,3; cis-1,2 trans-1,3; trans-1,2 cis-1,3; and trans-1,2 trans-1,3). All seven products gave 20 roughly the same peaks in their mass spectra in differing intensities. The following mass spectral data was for the first product isomer to elute from the gas chromatography (GC) column, and corresponds to one of the three main isomers of two perfluorocyclobutane 25 rings: m/e: 754 (36.4%); 593 (12.5%); 492 (14.1%); 415 (21.9%); 273 (27.7%); 242 (39.1%); 195 (21.5%); 173 (23.4%); 145 (100.0%); 126 (28.5%); 95 (23.1%); 92 (34.7%); 76 (57.6%); 64 (27.3%).

30 The second fraction also contained a small amount of material containing three perfluorocyclobutane rings, consisting of six isomers (cis-cis-cis, cis-cis-trans, cis-trans-cis, cis-trans-trans, trans-cis-trans, and trans-trans-trans) of 1,2-substituted

hexafluorocyclobutanes. Because of the small amount of this product present in the mixture, the corresponding products containing one or more 1,3-substituted hexafluorocyclobutane rings were not detected. The mass spectra of the six isomers showed roughly the same peaks in slightly differing intensities. The following mass spectral data was from the first product isomer of tri-perfluorocyclobutane material to elute from the GC column: m/e: 1024 (21.6%); 593 (16.3%); 492 (35.5%); 415 (17.6%); 281 (16.2%); 273 (16.4%); 242 (26.0%); 208 (15.9%); 207 (71.9%); 145 (100.0%); 92 (19.7%); 76 (26.8%).

In all cases, the primary products of cyclization were 1,2-substituted hexafluorocyclobutanes, with small amounts (1 to 2 percent) of 1,3-substituted hexafluorocyclobutanes observable by GC/MS, (except for the tri-perfluorocyclobutane material, of which only trace amounts were seen) the two being distinguished by a small peak at m/e = 100, corresponding to a fragment of  $CF_2=CF_2$  present in the mass spectra of the 1,2-substituted hexafluorocyclobutanes which was absent in the 1,3-substituted products. Absolute configurations of the different isomers were not assigned.

This example shows that a compound containing one trifluorovinyl group can be combined with a compound containing two trifluorovinyl groups, the mixture then being heated to cause cyclization of the trifluorovinyl groups to provide a fluid containing perfluorocyclobutane groups. Such fluids were of the

-48-

type useful as low dielectric hydraulic fluids or lubricants.

EXAMPLE 16: PREPARATION OF A FLUID POLYMER OF 1,3-BIS(TRIFLUOROVINYLOXY)BENZENE, 3-(1',1',2',2',TETRAFLUOROETHOXY)TRIFLUOROVINYLOXYBENZENE AND 1,3-BIS(1',1',2',2'-TETRAFLUOROETHOXY)BENZENE

A mixture (25 mL) consisting of 1,3-bis(trifluorovinyloxy)benzene (as prepared in Example 4) (26 percent), 3-(1',1',2',2',tetrafluoroethoxy)trifluorovinyloxybenzene (54 percent), 1,3-bis(1',1',2',2'-tetrafluoroethoxy)benzene (as isolated in Example 4) (15 percent), and tetraglyme (5 percent) was placed in a 100 mL round bottom flask and heated at reflux under nitrogen for 5 hours. The resulting viscous oil was checked by GC and was found to contain unreacted 1,3-bis(1',1',2',2',-tetrafluoroethoxy)benzene and tetraglyme, as well as mixtures of isomers of heavy components. After removal of the light, unreacted components, two fractions were cleanly separated by fractional distillation and each was analyzed by GC/MS.

The first fraction was found to contain primarily 1,2-bis(3'-[1",1",2",2"-tetrafluoroethoxy]phenoxy)hexafluorocyclobutane as two isomers (cis and trans substituted hexafluorocyclobutane) followed by small amounts (1-2 percent each) of two 1,3-substituted hexafluorocyclobutane products (cis and trans), all having roughly similar mass spectra. The following was the mass spectral data for the first isomer to elute from the chromatography column, and corresponds to one of the 1,2-substituted isomers: m/e: 580 (25.8%);

-49-

371 (11.3%); 321 (12.5%); 290 (23.4%); 270 (36.4%);  
243 (69.9%); 193 (100.0%); 95 (96.4%); 92 (55.9%);  
76 (26.7%); 64 (29.9%); 51 (21.9%).

The second fraction contained 1,3-bis(2'-[3"-  
5 {1"', 1"', 2"', 2"-tetrafluoroethoxy]phenoxy]hexa-  
fluorocyclobutyl)phenyl ether, primarily as three  
isomers of 1,2-substituted hexafluorocyclobutanes with a  
small amount of four isomers of the product with one  
1,2-substituted and one 1,3-substituted  
10 hexafluorocyclobutane ring. The seven isomers all gave  
roughly the same peaks in their mass spectra in  
differing intensities. The following mass spectral data  
was for the first isomer to elute from the GC column,  
and corresponds to one of the three main isomers of the  
15 product: m/e: 850 (24.7%); 540 (24.2%); 371 (41.5%);  
321 (12.9%); 301 (16.4%); 290 (33.9%); 270 (74.4%);  
243 (63.9%); 207 (24.1%); 193 (86.7%); 173 (14.8%);  
95 (100.0%); 92 (63.2%); 76 (71.8%); 64 (32.6%); 51  
20 (15.5%).

This example shows that a compound containing  
one trifluorovinyl group may be combined with a compound  
containing two trifluorovinyl groups in a solvent, the  
25 resulting mixture being heated to cause cyclization of  
the trifluorovinyl groups. Such fluids were of the type  
useful as low dielectric hydraulic fluids or lubricants.

EXAMPLE 17: PREPARATION OF 2,5-BIS(2-  
30 TRIFLUOROETHENYLOXY)HEXANE

Sodium hydride (16.5 g, 60 percent dispersion  
in oil, 0.41 mole) was transferred to an oven dried  
2 L 3-necked flask. Dry dimethyl formamide (DMF)

-50-

(400 mL) was added via syringe and the flask was fitted with a stirrer, thermometer, and septum. The mixture was stirred and cooled in an ice bath as 2,5-hexanediol (17.78 g, 0.15 mole) dissolved in 50 mL of dry DMF was added slowly via syringe. The septum was replaced with a pressure-equalizing addition funnel, and the mixture was stirred overnight. The mixture was cooled to -10 to -15°C with a dry ice/ethylene glycol bath, and 1,2-dibromotetrafluoroethane (TFDBE) (60 mL, 0.5 mole) was added dropwise to the stirring mixture. The 5 temperature of the reaction was maintained at -10 to -8°C. After one equivalent has been added, foaming was observed, which was allowed to subside before addition of TFDBE was resumed. Some slight foaming was observed for the rest of the reaction. As the reaction 10 approached completion, large amounts of solid 15 precipitate, which redissolve when the reaction was allowed to warm to 10°C.

20 The reaction mixture was partitioned between hexane and water. The hexane layer was washed with additional water to remove residual DMF, dried over magnesium sulfate, and concentrated to yield 63.15 g of orange oil. Volatile products were removed by vacuum 25 distillation to yield 36.12 g of colorless oil, which was then chromatographed on alumina with hexane to yield 19.23 g of 2,5-bis(2-bromotetrafluoroethoxy)hexane (26.9 percent yield) and 5.42 g of 2-(2-bromotetrafluoroethoxy)-5-(1,1,2,2-tetrafluoroethoxy)hexane as 30 confirmed by  $^{19}\text{F}$  NMR,  $^1\text{H}$  NMR and IR spectra of products.  $^{19}\text{F}$  NMR: (TFA)  $\delta$ -10.2 (t,  $J=6$  Hz), 8.8 (t,  $J=6$  Hz) HNMR: (TMS)  $\delta$ 1.32 (d, 6H,  $J=6$  Hz), 1.63-1.90 (m, 4H), 4.20-4.78 (m, 2H).

-51-

Zinc (1.93 g, 30 mmol) and 2,5-bis(2-bromo-tetrafluoroethoxy)hexane (3.45 g, 7.25 mmol) were weighed into a dry 100 mL 3-necked flask. Dry glyme (25 mL) was added via syringe and the resulting mixture was stirred and heated to reflux under nitrogen for 5 hours. The mixture was partitioned between pentane and water. The pentane extracts were dried over magnesium sulfate and concentrated to yield 2.11 g of pale yellow oil. Infrared analysis of this oil indicated the presence of some carbonyl containing impurities. The oil was dissolved in pentane and flushed through a column of neutral alumina to yield, after concentration, 1.33 g (65.8 percent yield) of the desired product. The title product was identified by 19F NMR, 1H NMR, and IR spectra. 19 F NMR: (TFA) 846.2 (ddd, J=90 Hz, J<sub>cis</sub> = 78 Hz, J<sub>HF</sub> = 2 Hz, OCF), 53.8 (d, J=78, =CF cis), 53.9 (d, J=90, =CF trans) 1H NMR: (TMS) 81.31 (d, J=6 Hz, 6H), 1.55-1.90 (m, 4H), 3.80-4.40 (m, 2H) IR: (CM-1) 1845 (CF=CF<sub>2</sub>), 20 1290 (B,C-O), 1130 (B, C-O).

The material was analyzed by DSC, and exhibited an exotherm of 500 Joules per gram (J/g) at 107°C.

25 EXAMPLE 18: PREPARATION OF METHYL 4-(2-BROMO-TETRAFLUOROETHOXY)BENZOATE, ITS CONVERSION TO TO 4-TRIFLUOROETHENYLOXYBENZOIC ACID AND THE BENZOYL CHLORIDE, AND USE OF THE CHLORIDE TO CHAIN EXTEND 30 POLYCARBONATE OLIGOMERS.

Methyl 4-hydroxybenzoate (304.3 g, 2 mole) was dissolved in 800 mL of methanol and was converted to the potassium salt by the slow addition of potassium hydroxide (132.02 g, 2 mol, 85 percent purity). The

-52-

resulting mixture was stirred and cooled as necessary to maintain the temperature below 50°C. The solvent was then removed by rotary evaporation and the crystalline salt was dried under vacuum overnight at 140°C.

5                   The dried salt was allowed to cool and transferred to an oven dried 2 L flask under nitrogen. The flask was fitted with a mechanical stirrer, thermometer, heating mantle, condenser and pressure-equalizing addition funnel. Dry dimethylsulfoxide 10 (DMSO) (550 g) was added and the mixture was stirred and warmed to 60°C as 1,2-dibromotetrafluoroethane (537 g, 2.06 mole) was added slowly. (No appreciable reaction was observed at lower temperatures.) Reaction 15 temperature was maintained at 65°C to 70°C for two hours after addition was complete. The mixture was then heated to 90°C and allowed to cool overnight.

20                  Product was isolated by extracting the mixture with 500 mL of water to remove salts and DMSO. The product separated as an orange oil which was washed with water to remove residual DMSO. (The upper aqueous layer was extracted with methylene chloride, and the methylene chloride solution was evaporated to yield about 40 g of 25 product which was added to the rest of the product prior to the water washes.) The product (623 g) was distilled at 85°C/0.3 mmHg (39.9 Pa) to yield 561 g of colorless oil, 85 percent yield. The product was identified by 19F NMR, 1H NMR, and IR spectra.

30                  To form a salt suitable for formation of the perfluorovinyl ether, another sample of methyl 4-(2-bromo-tetrafluoroethoxy)benzoate (66.25 g, 0.2 mole) was weighed into a 4-necked 500 mL round-bottomed

-53-

flask fitted with a condenser, thermometer, mechanical stirrer, and heating mantle. Methanol (300 mL) and sodium hydroxide (8.05 g, 0.2 mole) were added to form a mixture which was stirred and heated to reflux for three hours. A sodium carboxylate formed and 5 began to precipitate early in the reaction and was gelled into an almost solid mass after 1.5 hours. The mass was allowed to settle overnight and the solvent was then removed by rotary evaporation.

10 The sodium carboxylate was dissolved in warm water. A warm solution of zinc acetate (26.35 g, 0.12 mole) in 40 mL of water was added to precipitate the carboxylate as the zinc salt. The salt slurry was then cooled, and the zinc salt was filtered from the 15 solution and dried under vacuum to yield 65.6 g (94 percent yield).

20 The dried zinc salt was transferred to a dry 4-necked 500 mL round-bottomed flask containing zinc metal (10 mesh, 13.0 g, 0.198 mole). Dry glyme (160 mL) was added by a canula and the flask was fitted with a condenser, mechanical stirrer, and thermometer. The mixture was stirred and heated to reflux under nitrogen 25 overnight. The mixture was acidified by the addition of 18 mL of concentrated HCl, concentrated by rotary evaporation, and then partitioned between methylene chloride and water. The methylene chloride solution of the acid was dried over magnesium sulfate, filtered and 30 concentrated to yield 40.02 g of 4-trifluoroethenyl-oxybenzoic acid as white crystals (97.6 percent yield, m.p. 139-140°C). The product 4-trifluoroethenyl-

-54-

oxybenzoic acid was identified by  $^{19}\text{F}$  NMR,  $^1\text{H}$  NMR, and IR spectra.

5 To form the 4-trifluoroethoxybenzoyl chloride, 4-trifluoroethoxybenzoic acid (79.4 g, 0.36 mole) was transferred to a 1 L round-bottomed flask. Dry methylene chloride (250 mL) was added, and the resulting mixture was stirred under nitrogen as 10 oxalyl chloride (62.5 g, 0.49 mole) was added. The mixture was stirred overnight and then concentrated by rotary evaporation. The brown liquid was distilled at 60°C to 65°C/0.2 mmHg (26.6 Pa) to yield 82.94 g of colorless liquid (97.4 percent yield). The product was identified by  $^{19}\text{F}$  NMR,  $^1\text{H}$  NMR, and IR spectra.

15 To cap an oligomer, a low molecular weight polycarbonate oligomer (2000 MW) terminated with bisphenol A groups (7.5 g, about  $7.8 \times 10^{-3}$  mol of phenolic OH) was weighed into a 100 mL flask with the 20 trifluoroethoxybenzoyl chloride (1.84 g,  $7.8 \times 10^{-3}$  mole). Dichloromethane (30 mL) was added to dissolve the oligomer, and the mixture was stirred as triethylamine (0.81 g,  $8 \times 10^{-3}$  mole) was added via syringe. A fine white precipitate formed in the mixture 25 almost immediately. Dichloromethane was added to dissolve the precipitate, forming a dichloromethane solution which was extracted with water to remove triethylamine hydrochloride. The dichloromethane solution was dried over 4A molecular sieves, and 30 concentrated to yield 9.06 g (100 percent yield) of oligomer capped with trifluoroethoxybenzoyl groups. Structure was verified by  $^{19}\text{F}$  NMR (trifluorovinyl ether pattern),  $^1\text{H}$  NMR (2 protons of the aromatic benzoate were shifted downfield to 8-8.3 ppm from the aromatic

polycarbonate protons), and FT-IR (C=O stretch at 1739 cm<sup>-1</sup>, distinct from the C=O stretch of polycarbonate at 1774 cm<sup>-1</sup>).

5 A sample of the capped oligomer was heated to 300°C in a DSC apparatus to effect chain extension. The sample was cooled and reheated to determine the T<sub>g</sub>, which was observed at 140.4°C (representative of high molecular weight polycarbonate). For comparison, a 10 sample of the uncapped oligomer heated to 300°C, cooled, and reheated, exhibited a T<sub>g</sub> of only 106.8°C. The increase of 33.6°C in the T<sub>g</sub> was attributed to the 15 production of high molecular weight polycarbonate through the thermal cyclodimerization of the trifluorovinyl ether groups.

EXAMPLE 19: REACTION OF 4,4'-BIPHENOL AND TRIFLUOROVINYLOXYBENZOYL CHLORIDE

20 Dihydroxybiphenyl (0.7888 g, 0.00423 mole) was placed in a dry 250 mL round bottom flask with a magnetic stirring bar. The flask was capped with a rubber septum. Dry methylene chloride (25 mL) and trifluorovinyloxybenzoyl chloride as prepared in Example 25 18 (2.000 g, 0.00846 mole) were each added to the flask via syringe. The mixture was stirred as triethylamine (0.86 g, 0.0085 mole) was added dropwise. The mixture was stirred at room temperature for 2 hours, then 30 filtered. A white precipitate was obtained and washed several times with methylene chloride to remove residual triethylamine hydrochloride. A white crystalline product was obtained and has a melting point of 225°C to 228°C. Qualitative solubility tests indicate that this product was nearly insoluble in methylene

-56-

chloride, acetone, acetonitrile, hexane, methanol, water and benzene, only slightly soluble in hot tetrahydrofuran, and moderately soluble in carbon tetrachloride.

5                   Infrared analysis (using a potassium bromide (KBr) pellet) gave the following spectrum (reported in cm<sup>-1</sup>): 1830, indicative of a trifluorovinyl group; 1723, indicative of a benzoate ester; 1600 and 1495, indicative of aryl carbon-carbon double bond; 1315 and 10 1267, indicative of carbon-fluorine bonds.

15                  Thermal analysis (DSC) of the monomer indicated a crystalline melt beginning at 223°C, followed immediately by a slight exotherm as the monomer 15 underwent polymerization. A second scan of the sample showed no thermal activity up to and including 350°C.

20                  The melted monomer exhibited possible liquid crystalline behavior during it's short-lived melt phase. As viewed under a cross-polarized light microscope, the melted monomer phase (at 230°C) exhibited birefringence suggestive of liquid crystalline behavior, followed by rapid polymerization to a crystalline solid. This solid 25 did not melt, but underwent discoloration and apparent decomposition when heated in air at temperatures above 400°C.

EXAMPLE 20: SYNTHESIS OF 1-BROMO-2,4-BIS(2-  
30                    TRIFLUOROETHENYLOXY)BENZENE FROM RESORCINOL

Resorcinol (412.9 g, 3.75 mole) was dissolved in 1800 mL of DMSO and 670 mL of toluene to form a mixture in a 3-necked, 5 L flask fitted with an overhead

stirrer, moisture trap and condenser, and nitrogen sparge. The mixture was stirred and sparged with nitrogen as potassium hydroxide (495.1 g, 7.5 mole) was added in 5 g portions. The mixture was then heated to reflux to remove water by azeotropic distillation.

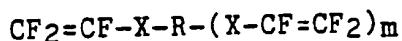
5 After the water was removed, the mixture was cooled to 15°C as 1,2-dibromotetrafluoroethane (2144 g, 8.25 mole) was added rapidly, and the mixture was stirred overnight. The mixture was then stirred and heated to 90°C for three hours. The mixture was then cooled and 10 diluted with an equal volume of water. The product separated as an oily lower layer, which was fractionally distilled under vacuum to yield 190.3 g of 1-(2-bromo-tetrafluoroethoxy)-3-(1,1,2,2-tetrafluoroethoxy)benzene (3 percent yield), 895.5 g of 1,3-bis(2-bromotetra-fluoroethoxy)benzene (51 percent yield), and 340.8 g of 15 1-bromo-2,4-bis(2-bromotetrafluoroethoxy)benzene (17 percent yield). The products were identified by 19 F NMR, H NMR, and IR spectra.

20  
1-Bromo-2,4-bis(2-bromotetrafluoroethoxy)benzene (18.06 g, 35 mmole) was added dropwise to a hot (110°C) mixture of zinc (4.74 g, 72.5 mmole) in dry tetraglyme (20 mL). Product 1-bromo-25 2,4-bis(trifluoroethoxy)benzene was fractionally distilled from the mixture under vacuum (95°C to 100°C/1 mmHg (133 Pa), 6.57 g, 59 percent yield). The product was identified by 19 F NMR, H NMR, and IR spectra.

-58-

1. A compound having at least two perfluorovihyl groups and having a structure represented by the following Formula I:

Formula I



5 wherein R represents an unsubstituted or inertly substituted hydrocarbyl group; each X is independently selected from the group consisting of groups having at least one non-carbon atom between R and  $-\text{CF}=\text{CF}_2$ ; and m is an integer of from 1 to 3.

10

2. The compound of Claim 1 wherein each X is selected independently sulfur atoms, sulfoxide, sulfone, an oxygen atom, carboxylic and thiocarboxylic ester groups, phosphines, carbonyl and thio carbonyl groups; 15 seleno; telluro; nitrido; silanediyl, trisilanediyl, tetrasilanetetrayl, siloxanediyl, disiloxanediyl, trisiloxyl, trisilazanyl, or silylthio groups; boranediyl or methylboranediyl groups.

20

3. The compound of Claim 1 wherein R is an unsubstituted or inertly substituted aromatic group, having from 6 to 25 carbon atoms.

-59-

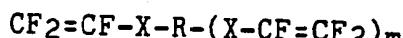
4. The compound of Claim 3 wherein the aromatic group is biphenylene; phenylene; 9,9'-diphenylfluorene, oxydiphenylene; thiadiphenylene; 1,3,5-triphenylenebenzene; 1,3,5-(2-phenylene-2-propyl)bezene; 1,1,1-triphenylenemethane; 1,1,2,2-tetraphenylene-1,2-diphenylethane; bis(1,1-diphenyleneethyl)benzene; 1-(2-phenylene-2-propyl)-4-(1,1-diphenylene ethyl)benzene; 1,1,1-triphenyleneethane; 2,2-diphenylene propane; 2,2-diphenylene, 1,1,1,3,3,3-hexafluoropropane; 1,1-diphenylene-1-phenylethane; naphthalene; and anthracene.

5. A polymer prepared by thermally forming perfluorocyclobutane rings from compounds of any one of Claims 1 to 4.

15

6. A process for preparing a compound having at least two perfluorovinyl groups and represented by the following Formula I:

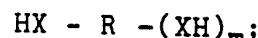
20 Formula I



wherein each X is independently -0-, -S-, -SO- or -SO<sub>2</sub>-; and R is a hydrocarbyl group which group is 25 unsubstituted or inertly substituted, by a process comprising the steps of:

30 (a) forming a salt having anion corresponding to a compound represented by the following Formula II:

Formula II



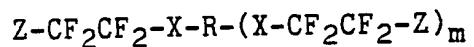
wherein X, R and m are as defined for Formula I;

-60-

(b) reacting the salt formed in step (a) with a 1,2-dihalo-1,1,2, 2-tetrafluoroethane wherein the halo groups are iodine, bromine, chlorine or mixtures thereof, at least one halo group being bromine or iodine, to form a compound represented by the following

5 Formula III:

Formula III



wherein X, R and m are as defined for Formula I and each  
10 Z is independently iodine or bromine; and

(c) eliminating the halogen atoms represented by Z to form the perfluorovinyl compound represented by  
15 Formula I.

15

20

25

30



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C07C 43/225, 43/17, 323/09 C08F 16/12, 128/04		A3	(11) International Publication Number: WO 90/15043 (43) International Publication Date: 13 December 1990 (13.12.90)
(21) International Application Number: PCT/US90/03154 (22) International Filing Date: 4 June 1990 (04.06.90)		(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent).	
(30) Priority data: 364,665 9 June 1989 (09.06.89) US		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).		(88) Date of publication of the international search report: 21 March 1991 (21.03.91)	
(72) Inventors: BABB, David, A. ; 419 Narcissus, Lake Jackson, TX 77566 (US). CLEMENT, Katherine, S. ; 126 Daisy, Lake Jackson, TX 77566 (US). EZZELL, Bobby, R. ; 1310 Ashly court, Midland, MI 48640 (US).			
(74) Agent: PRIETO, Joe, R.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).			

## (54) Title: PERFLUOROVINYL COMPOUNDS

## (57) Abstract

The present invention is directed to compounds having at least two perfluorovinyl groups and having a structure represented by the following formula (I):  $CF_2=CF-X-R-(X-CF=CF_2)_m$ , wherein R represents an unsubstituted or inertly substituted hydrocarbyl group; each X is independently selected from the group consisting of groups having at least one non-carbon atom between R and  $-CF=CF_2$ ; and m is an integer of from 1 to 3. Polymers formed from such compounds are also prepared. The compounds are preferably prepared by a process comprising the steps of: (a) forming a salt having anion corresponding to a compound of the following formula (II):  $HX-R-(XH)_m$ , wherein X, R and m are as defined for formula (I); (b) reacting the salt formed in step (a) with a 1,2-dihalo-1,1,2,2-tetrafluoroethane wherein the halo groups are iodine, bromine, chlorine or mixtures thereof, at least one halo group being bromine or iodine, to form a compound of the following formula (III):  $Z-CF_2CF_2-X-R-(X-CF_2CF_2-Z)_m$ , wherein X, R and m are as defined for formula (I) and each Z is independently iodine or bromine; and (c) eliminating the halogen atoms represented by Z to form the perfluorovinyl compound represented by formula (I).

## DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

### FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MC	Monaco
AU	Australia	FI	Finland	MC	Madagascar
BB	Barbados	FR	France	ML	Mali
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Fasso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GR	Greece	NL	Netherlands
BJ	Benin	HU	Hungary	NO	Norway
BR	Brazil	IT	Italy	PL	Poland
CA	Canada	JP	Japan	RO	Romania
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
DE	Germany	LU	Luxembourg	TD	Chad
DK	Denmark			TG	Togo
				US	United States of America

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/03154

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC<sup>5</sup> C 07 C 43/225, 43/17, 323/09, C 08 F 16/12, 128/04

## II. FIELDS SEARCHED

Classification System	Minimum Documentation Searched <sup>7</sup>	
	Classification Symbols	
IPC <sup>5</sup>	C 07 C 43/00, C 08 F 16/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		

## III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US, A, 3114778 (C.G. FRITZ) 17 December 1963 see the whole document --	1,2
X	FR, A, 1481730 (DU PONT) 19 May 1967 see abstract; examples --	1,2
X	Chemical Abstracts, volume 86, no. 19, 9 May 1977, (Columbus, Ohio, US), O. Paleta et al.: "Haloacrylic acids. VI. Ethylene glycol bis (trifluoro- acrylate)", see pages 503,504, abstract 139369w, & Sb. Vys. Sk. Chem.-Technol. Praze, Org. Chem. Technol. 1976, C23, 5-11 -----	1,2

\* Special categories of cited documents: <sup>10</sup>

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

## IV. CERTIFICATE

Date of the Actual Completion of the International Search

28th November 1990

Date of Mailing of this International Search Report

18 FEB 1991

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

Mm N. KUIPER

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND incompletely searchable

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.  Claim numbers ..... because they relate to subject matter not required to be searched by this Authority, namely:

2.  Claim numbers ..... \*, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

\* 1-5

In claim 1 the definition of X is unclear. In claim 2 when X is carbonyl or thiocarbonyl there is no non-carbon atom between R and  $CF=CF_2$  (art. 6 PCT). The search has been based on the examples

3.  Claim numbers....., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this International application as follows:

1. Claims 1-5 : Perfluorovinyl containing compounds and polymers
2. Claim 6 : Process to prepare new and known compounds

1.  As all required additional search fees were timely paid by the applicant, this International search report covers all searchable claims of the International application.

2.  As only some of the required additional search fees were timely paid by the applicant, this International search report covers only those claims of the International application for which fees were paid, specifically claims:

3.  No required additional search fees were timely paid by the applicant. Consequently, this International search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

1-5

4.  As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

The additional search fees were accompanied by applicant's protest.

No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

US 9003154

SA 38108

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 06/02/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3114778		None	
FR-A- 1481730		DE-A- 1645142 22-10-70	
		DE-A- 1793181 01-07-71	
		GB-A- 1108128	
		NL-A- 6607678 05-12-66	

**THIS PAGE BLANK (U.S.PTO)**